THE CHEMICAL DURABILITY OF PORCELAIN ENAMELS

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RALPH LA VERNE COOK
B.S., University of Alabama, 1934
M.S., University of Illinois, 1940

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
ENGINEERING IN THE GRADUATE SCHOOL OF
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I. Introduction

The purpose of the investigation was to determine the chemical durability of commercially representative porcelain enamels to the attack of various inorganic and organic acids, alkalies, and selected salt solutions at room temperature and at boiling temperatures. The porcelain enamel sufraces which were selected for study included a ground coat enamel, a fluoride white cover enamel, a sign blue cover enamel, a blue zirconium cover enamel, an acid-resistant white cover enamel and an acid-proof cover enamel. The actual loss in weight per unit sufrace area at selected time intervals was used as a measure of the attack of the different chemical solutions on the various porcelain enamel surfaces.

II. Previous Investigations

In reviewing the literature on the chemical durability of porcelain enamels one is impressed by the extensive number of tests and the variety of conditions under which these tests were run. These various tests can be classified into three main groups; the grain test, the spot test and the loss in weight test.

In the grain test, a weighed amount of the powdered enamel frit is subjected to acid for a definite length of time. The enamel powder is then filtered off and reweighed, the loss in weight representing the amount of acid attack. This test has been used by Poste[1], Uchida and Arimoto,[2], Andrews[3] and others.

The spot test is an actual simulated service test and consists of placing several drops of acid on the fired porcelain enamel surface, and noting the degree of attack after a definite time interval. The spot test has been used in various investigations by Andrews[3], Shaw[4], Gautsch,[5], Spencer-Strong[6] and was adopted as a standard test by the Porcelain Enamel Institute[7].

In the loss in weight test, weighed enamel test pieces are exposed to acid action for a definite time period, and then reweighed. The weight loss per unit area is taken as the index of acid attack. This test has been used by a large number of investigators, including Shaw[8], Landrum[9], Collins[10] and Staley[11].

The New South Wales Test[12], the British Standard Test[13] and the Enameled Utensils Manufacturing Council[14] have developed standards based on the loss in weight method.

III. Experimental Procedure

In this study the loss in weight test was used in determining the chemical attack on the various enamel surfaces. The porcelain enamel compositions, in general, were smelted in either a crucible or a rotary smelter. The frits were milled with the usual mill additions to a fineness of six to eight grams, from 100 grams of frit, on a No. 200 sieve.

The test containers used in this investigation consisted of shallow-drawn cylindrical shapes 2.5 inches in diameter and 1.75 inches in depth with a flange 0.625 inches around the top. The cup-shaped containers were properly cleaned and pickled in the usual commercial manner for the preparation of sheet metal parts for enameling. The ground coat enamel was applied by slushing, the test shapes dried, and then fired in an automatically controlled electric resistance furnace. In general, two separate coats of each cover enamel were applied and fired on the ground coated containers. In every case, the finished containers were inspected critically for surface irregularities and defects, and further tested by the Cecso spark tester in order to assure representative surface characteristics.

Different concentrations of the four mineral acids (hydrochloric, sulphuric, nitric and phosphoric), various organic acids, including oxalic, citric, acetic, tartaric, lactic, malic, pyrogallic, and carbolic acids, solutions of sodium hydroxide, and several salts were used in this investigation.

In determining the resistance of the various enamel surfaces to the attack of the different chemical solutions the following general procedure was used: first, the effect of the chemical solutions at room temperature was tried, and where the attack was appreciable the loss in weight was determined at time intervals of 1, 2½, 5, 10, 20, 40, 80, and 180 hours, or until a surface fracture occurred; in the other cases, where the total loss in weight at room temperature was low, the loss in weight was determined at boiling temperatures, at time intervals of 10, 25, 50, and 100 hours. The test containers were carefully weighed

on an analytical balance to the nearest 0.0001 grams. Exactly 100 c. c. of the test solution was measured into the weighed container and after standing for a definite time interval, the solution was removed, the container dried and reweighed. In studying the attack at boiling temperatures, a long-tube reflux condenser was clamped on the containers, and the samples boiled vigorously on an electric hot-plate for a definite time interval. The solution was then removed and the test sample reweighed.

IV. Results and Discussion

The porcelain enamel surfaces were exposed to the chemical action of the various solutions which were measured into the test containers. After a definite time the samples were reweighed, and the loss in weight, expressed in grams per square inch, determined for each test condition. The chemical durability curves of loss in weight vs. time were plotted.

A. *The Effect of Inorganic Acids*

The effects of the different concentrations of the four mineral acids on the various enamel surfaces can be summarized by considering (1) the effect on the ground coat enamel, (2) the effect on the fluoride cover enamel and (3) by comparing the other enamels with these typical surfaces. On the ground coat enamel surfaces the concentrated acids, with the exception of hydrochloric acid showed only slight attack; the ten and twenty or twenty-five percent acid solutions showed sufficient attack to break through the surface in a comparatively short period of time; and the one percent solutions showed moderate attack in the first few hours with practically no increased attack thereafter. With the fluoride surfaces, the concentrated acids with the exception of sulphuric acid showed a moderate to pronounced degree of attack; the one percent acid solutions showed appreciable initial attack, with a very slight increase thereafter; and the intermediate concentrations showed decided attack in every case. In general, the attack on the fluoride enamels is at least a 2 to 3-fold increase over that shown by the same solution on the ground coat enamels. The antimony cover enamel and the sign blue cover enamel showed the same general characteristics as the ground coat enamel. The zirconium white cover enamel and the blue zirconium cover enamel were attacked similarly to the fluoride cover enamel.

The acid-resistant and acid-proof enamel showed practically no attack at room temperature. At boiling temperatures, these same surfaces were attacked to a moderate degree. The acid-resistant enamel was less resistant to attack than the acid-proof enamel.

B. *The Effect of Organic Acids*

The comparative chemical attacks of ten percent solutions of the selected organic acids on the various enamel surfaces were determined. In summarizing the general effect of the organic acids on the nonacid-resisting enamel surfaces at room temperature, it is to be noted that (1) a ten percent solution of oxalic acid showed almost as much chemical attack as the ten percent solutions of the mineral acids, (2) ten percent solutions of citric acid, tartaric acid, lactic acid and malic acid showed about the same general type and amount of attack on the different enamel surface, (3) a ten percent solution of acetic acid was relatively weak when compared with the aforementioned acids, and (4) the ten percent solutions of pyrogallic acid and carbolic acid showed almost no attack on the porcelain enamels. The acid-resistant and acid-proof enamel surfaces were quite resistant to the attack of the organic acids at room temperature.

At boiling temperatures, the different organic acids showed about the same order of attack, but far less total attack, on the acid-resistant and acid-proof enamel surfaces as was indicated on the nonacid-resisting surfaces at room tempreature. The acid-resistant enamel was attacked to a greater degree by the boiling organic acids than the acid-proof enamel surfaces.

C. *The Effect of Alkalies and Salts.*

In general, at room temperature, the various enamel surfaces were not appreciably affected by either an alkaline solution or the selected salt solutions over a relatively long time period. A boiling ten percent solution of sodium hydroxide showed pronounced and rapid attack on all of the enamel surfaces.

The loss in weight, after a boiling salt solution was in contact with the enamel surface for 100 hours, was determined. All eight of the enamel surfaces were resistant to the action of a ten percent sodium chloride solution. The acid-proof enamel, the

acid-resistant enamel, the sign blue enamel, and the ground-coat enamel were attacked to an appreciable extent by the ten percent sodium carbonate solution, while the other four enamel surfaces were only slightly affected. The ten percent solution of sodium borate showed about equally low attack on all the enamels. The ten percent solution of sodium bi-carbonate showed erratic results, some surfaces being attacked appreciably while others were practically unaffected. The ten percent solutions of magnesium sulphate, sodium sulphate, sodium sulphite, and sodium nitrate, showed relatively low attack on the enamel surfaces. The solution of tri-sodium phosphate showed decided attack on all of the enamels. The attack of the di-sodium acid phosphate solution was considerably less than that of the tri-sodium phosphate. The ten percent solution of zinc chloride showed the greatest attack on the zirconium and fluoride white cover enamels, and on the sign blue cover enamel. The ten percent solution of aluminum chloride showed appreciable attack on practically every surface, except the acid-resistant and acid-proof enamels. When the ten percent solution of aluminum chloride was in contact with the sign blue cover enamel the container showed a gain in weight due to the deposition of an adherent residue.

V. Analysis of Results

At the end of each of the previous sub-sections the results were summarized and interpreted. As a further aid in analyzing the results of the attack of the various chemical solutions on the different enamel surfaces, the mechanism and nature of the chemical action can be considered as (A) the effect of acid on the nonacid-resistant enamel surfaces, (B) the effect of acid on the acid-resistant enamel surfaces, (C) the effect of alkalies on porcelain enamels, and (D) the effect of the selected salt solutions on the various enamel surfaces.

A. *The Effect of Acid on the Nonacid-Resistant Surfaces.*

In general when an organic or inorganic acid is brought in contact with the nonacid-resistant surfaces, the gloss is progressively destroyed, a decided etch is imparted to the surface, and finally the enamel coating is destroyed until only a fine powdery dust remains.

In explaining the action of the various organic and inorganic acid solutions on the different porcelain enamel surfaces, one might postulate that since silica is the predominant constituent in porcelain enamels, the silica would form a relatively loose random structural arrangement in which the other constituents such as B, Al, Na, K, Ca, and others would either replace silicon or be distributed at random in the holes in the structural network. When the porcelain enamel coating is subjected to acid attack either (1) the more soluble materials such as Na, K, B, and others would be progressively leached out of the structural network leaving a silica enriched layed or (2) the entire structure would be systematically and uniformly attacked and decomposed. In the first case in which a silica enriched layer would be left in contact with the acid solution the silica would remain as a hydrated or gel-like material. The silica gel upon being dried would shrink and pull apart thus causing the sharp jagged corners as observed in the photomicrographs of the different enamel surfaces. It is to be noted that the four decidedly different nonacid-resisting enamels, the ground coat, the fluoride cover, the antimony cover, and the sign blue cover enamel all show this characteristic. Further, the size of the pattern is dependent on the actual amount of acid attack which in turn is dependent on (1) the enamel composition, (2) the concentration and kind of acid, and (3) the time interval during which the acid was in contact with the enamel surface. The other two nonacid-resistant surfaces, the zirconium white cover enamel and the blue zirconium enamel, appear to be attacked as in the second case in which the structure is systematically decomposed, and the silica completely removed rather than left as a layer of silica gel.

B. *The Effect of Acid on the Acid-Resistant Enamel Surfaces.*

When an inorganic or organic acid is brought in contact with the acid-resistant type of surface, there may be a slight loss in specular reflection or an iridescence may be imparted to the surface. With additional attack, the acid solution penetrates the surface at some inhomogeneity which then appears as a lighter opaque area. With further attack, the metal surface below may be exposed.

In explaining the action of acid on these highly acid-resistant

surfaces, one might consider the silica as forming a dense close-packed structural arrangement in which the other elements are distributed in the holes in the network. When exposed to acid, the silica structure is not disturbed, but the elements in the interstices of the network are leached out.

C. *The Effect of Alkalies on Porcelain Enamels.*

Alkaline solutions showed only slight attack on the porcelain enamel surfaces at room temperature. At boiling temperatures, the alkaline solutions showed rather rapid attack on all the enamel surfaces. The enamel coating is progressively dissolved by the boiling alkaline solution which leaves the surface porous and etched.

The alkaline solution appears to attack and destroy the silica structure by dissolving the silica along with the other components in the enamel surface.

D. *The Effect of Salt Solutions on Porcelain Enamels.*

In analyzing the effect of the salt solutions on the various enamel surfaces, it was noted that the surfaces showed, either (1) no attack, (2) a slight iridescence or loss of gloss, (3) a decided etch, or (4) in some cases, the deposition of a hard, insoluble residue on the enamel coating. In explaining the action of the salt solutions, it is indicated, that they are dependent on one or more of the following factors: (1) the nature of the ions released by the hydrolysis of the salts, (2) the degree of dissociation of the respective ions, (3) the effect of secondary dissociation, (4) the effect of ions leached out or released from the enamel coating, and (5) the deposition of insoluble precipitates either in the solution or on the enamel surface.

VI. Conclusions

1. Many previous investigators have used the loss in weight method, with a definite but single time period, in determining acid attack. The results of this present investigation show that a far more accurate picture of chemical action is obtained, when the loss in weight is measured after several successive time periods, and the chemical durability curve—loss in weight against time, plotted.

2. The loss in weight method is a very satisfactory means of studying the chemical attack of the inorganic and organic acids, the alkalies, and to a lesser extent the salt solutions, at room temperature and at boiling temperatures.

3. The ground coat enamel is as resistant or more resistant to acid attack than the other nonacid-resisting enamels.

4. The antimony white cover enamel is considerably more resistant to acid attack than either the fluoride white cover enamel or the zirconium white cover enamel.

5. In general, at room temperature, the nonacid-resisting enamels are attacked only slighly by concentrated sulphuric or phosphoric acids, are attacked more by concentrated nitric acid, and are appreciably attacked by concentrated hydrochloric acid.

6. The less concentrated mineral acid solutions: the twenty, ten and one percent strengths all show appreciable to rapid attack, at room temperature, on practically all of the nonacid-resisting enamel surfaces.

7. Several of the organic acids show an appreciable amount of attack, at room temperature, on the nonacid-resisting enamels.

8. Porcelain enamel surfaces are quite resistant to chemical attack by alkalies and salt solutions, at room temperature.

9. At room temperature, acid-resistant white cover enamels are very resistant to the attack of inorganic and organic acids.

10. Acid-resistant white cover enamels are attacked to a moderate extent by the boiling mineral acids (sulphuric, hydrochloric, nitric and phosphoric), to a slightly less extent by boiling oxalic acid, to an even less extent by boiling solutions of citric, tartaric, malic and lactic acids, while the boiling solutions of acetic, pyrogallic and carbolic acids show almost no attack.

11. The acid-proof or chemical enamel is approximately three times as resistant to acid attack at boiling temperatures as the acid-resistant white cover enamels.

12. Ground coat enamels and all cover enamels, including acid-resistant and acid-proof, show equally low resistance to the attack of a boiling sodium hydroxide solution.

13. The action of the boiling salt solutions on the various enamel surfaces is quite specific. In general, salts, which upon hydrolysis give a decided alkaline reaction, show appreciable attack on all of the enamel surfaces; and salts, which upon hydrolysis give a distinct acid reaction, show practically no attack on the acid-resisting surfaces, but they show variable attack on the nonacid-resisting enamels.

14. In interpreting the mechanism of chemical attack on porcelain enamels, it is indicated, that since silica is the predominate constituent in these coatings, the silica would form a relatively loose random structural arrangement in which the constituents such as B, Al, Na, K. Ca and others would either replace silicon or be distributed in the interstices of the structual network. When the porcelain enamel coating is subjected to chemical attack either (1) the more soluble material would be selectively leached out of the network leaving a silica enriched layer, or (2) the silica structure would be attacked and decomposed. In the former, the silica enriched layer would be present as a gel-like material, which upon drying, would shrink and pull apart, leaving the characteristic pattern of attack.

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Vita

Ralph La Verne Cook was born in Erie, Pennsylvania, on April 17, 1912. He received his primary education in public schools of Erie and Wesleyville, Pennsylvania.

He entered the University of Pittsburgh in the fall of 1930 and transferred the following year to the University of Alabama. Here he received the degree of Bachelor of Science in Chemistry, Metallurgy and Ceramics in May, 1934. From then until 1938 he was employed as Ceramic Engineer in the Works Laboratory, Erie Works, of the General Electric Company. In the fall of 1938 he accepted a position as Instructor, in the Department of Ceramic Engineering, at the University of Illinois. At the same time he enrolled in the Graduate School, and received the degree of Master of Science in Ceramic Engineering in 1940. From 1938 until the present time he has served as Instructor and later as Associate in the Department of Ceramic Engineering at the University of Illinois.

The author is a member of Sigma Xi, Keramos, the American Ceramic Society, Gamma Sigma Epsilon, Chi Beta Phi, and the Alpha Chi Sigma fraternity.

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